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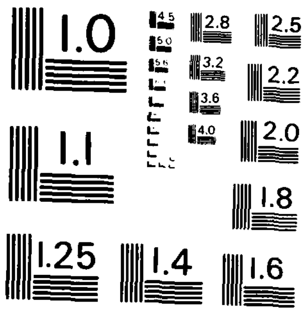

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AFATL-TR-82-40

Effects of Uranium Oxides on Some of the Algae Native to Eglin Air Force Base, Florida

Temd R Deason

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AD A124247

JUNE 1982

FINAL REPORT FOR PERIOD FEBRUARY 1977–SEPTEMBER 1979

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Air Force Armament Laboratory

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Uranium Uptake	Turkey Creek
Uranium Accumulation	Eglin Air Force Base Reservation
Depleted Uranium	Uranium Oxides

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Population studies were made for algae collected from creeks on the Eglin Air Force Base reservation in Northwest Florida. Cultures of several of the algal species found in the creeks were isolated and exposed to various concentrations of UO_2 and U_3O_8 to determine how the algae responded, how much uranium they took up, and what uptake mechanism was involved. Factors related to mobility of uranium on the reservation are discussed.

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PREFACE

The Air Force contract directly related to this report is Contract Number F08635-77-C-0047. This report covers the period from February 1977 to September 1979. The Air Force program monitor for this program was Ms Sandra Lefstad of the Environics Office, Air Force Armament Laboratory, Armament Division, Eglin Air Force Base, Florida 32542. Contractor for this project was Temd R. Deason, Department of Biology, University of Alabama, University, Alabama 35486.

Some laboratory data were generated in part by Dr. Gary L. Butler and Ms Janet Hawkins, Department of Biology, University of Alabama. Their assistance in this project is gratefully acknowledged. Collection of field data was made possible by the assistance of Ms Lefstad and Mr. Richard Crews of the Environics Office. This assistance and valuable suggestions obtained through consultations with these individuals are also gratefully acknowledged.

Verifications of diatom identifications were facilitated by Dr. Charles Reimer of the Academy of Natural Sciences of Philadelphia who generously donated his time and laboratory space for this endeavor.

The Public Affairs Office has reviewed this report, and it is releasable to the National Technical Information Service (NTIS), where it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

FOR THE COMMANDER

Joe A. Farmer

JOE A. FARMER
Chief, Environics Office

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SECTION I

INTRODUCTION

Some firing ranges on Eglin Air Force Base Reservation utilize depleted uranium armour-piercing ammunition. When the ammunition strikes the target, some of the uranium falls to the ground and is subject to be transported to nearby streams. This study is a combined field and laboratory investigation of the algae in streams bordering two of these ranges to determine what algae are present, at what rate the uranium could be transported, how toxic uranium is to the algae, and the mechanisms and quantities involved in uranium uptake by the algae.

DESCRIPTION OF GEOGRAPHICAL AND ENVIRONMENTAL FACTORS

a. General Area

The Eglin AFB Reservation is located in Northwest Florida where it occupies a portion of Santa Rosa Island, Okaloosa Island, the southeastern part of Santa Rosa County, the southern half of Okaloosa County, and the southwestern quarter of Walton County. It covers an area of approximately 750 square miles. To the south the reservation is adjacent to Choctawhatchee Bay and the Gulf of Mexico, while to the north it is bordered roughly by the Yellow River and Titi Creek. Alaqua Creek.

The reservation lies on generally level or gently rolling terrain, all under 300 feet in elevation and sloping to sea level on the west and south. It is drained by small tributaries of the Yellow River and Alaqua Creek and by smaller streams that flow directly into Pensacola Bay and Choctawhatchee Bay. The valleys of these streams often are steep sided and terminate abruptly. The soil of most of the reservation consists of somewhat excessively drained, deep, acid sands of the Lakeland series. In the stream bottoms, the soils are much more heavily organic.

b. Rocky and Turkey Creeks

These two streams originate on the Eglin Reservation and drain into Choctawhatchee Bay. Rocky Creek is longer and has greater water flow near its discharge point. Rocky Creek drains some land contaminated with low concentrations of non-native depleted uranium. Turkey Creek is free of any non-native uranium and was selected as a control stream to compare with Rocky and Bull Creeks. The collecting site on Rocky Creek was unshaded, shallow, and with little submerged vegetation other than grasses. Some seepage enters the clear stream from an adjacent swamp-like area bringing some organic material with it. The Turkey Creek site was shaded by overhanging trees, and the clear water was as much as a meter deep in some places, covering some submerged trees and roots.

c. Bull Creek

Bull Creek drains Range C-64 on the Eglin Reservation. It is a clear oligotrophic stream with a sandy bottom and a depth of less than one meter at the collecting sites. Site 64-1 is near a bridge on Range Road 211. Site 64-2 is on TA C-64.

SECTION II

FIELD STUDIES

1. INTRODUCTION

Site visits for the purpose of measuring physical properties of water and collecting algae at the designated sites were made on the following dates: 24 February 1977, 4 May 1977, 2 June 1977, 28 June 1977, 16 February 1979, 2 April 1979, 1 May 1979, 21 May 1979, 18 June 1979, 2 August 1979, and 22 August 1979.

2. PHYSICAL MEASUREMENTS OF STREAM WATER

These measurements included pH, temperature, and dissolved oxygen (DO). The visiting days were usually during clear weather not following excessive rainy periods and there was no measurable turbidity. Measurements are recorded in Tables 1 and 2.

Water temperature ranged from a low of 17.0°C at the Rocky Creek site in February 1977, to a high of 23.0°C at the Turkey Creek site in June 1977. Dissolved oxygen ranged from 7.0 parts per million (ppm) in Turkey Creek in June 1977 to 9.4 ppm in Rocky Creek in May 1977. The pH ranged from 4.9 at sites 64-1 and 64-2 in May 1979 to 5.4 in Turkey Creek during February 1977.

3. COLLECTION OF ALGAE AT STREAM SITES AND ISOLATION OF SELECTED SPECIES INTO AXENIC CULTURES

a. Methods

Several collections of the epiphytic flora were made in sterile glass jars at each site. These were returned to the laboratory at the University of Alabama on ice in insulated containers one day after the collection. Each collection was examined microscopically and the algae (exclusive of diatoms) were identified to genus (Table 3). Permanent diatom slides were made for later identifications to species and variety (Table 4).

Several one-milliliter (ml) aliquot samples were added to 10 ml of one of each of the following media in test tubes: Bristol's Inorganic Salt Medium (Deason and Bold, 1960), and FW-1 Medium (Lewin, 1966). These tubes were placed on illuminated culture racks in the laboratory at the University of Alabama for approximately 4 weeks. At this time many of the tubes contained significant quantities of mixed algae as well as bacteria. By dilution and plating techniques, several organisms were obtained in unialgal cultures, and eventually were placed into axenic cultures (Table 5).

These algae, isolated from the designated sites, were utilized in laboratory studies to determine their ability to grow in the presence of uranium compounds, and the amount of absorption and adsorption by their cells.

b. Results

The number of algal species collected from Rocky Creek always exceeded the number collected from Turkey Creek (Tables 3 and 4). This probably was due to the shaded collecting sites on Turkey Creek. There was no significant difference in numbers of species collected from Sites 64-1 and 64-2 (Tables 3 and 4). These sites received approximately the same amount of light. No significant seasonal differences were noted in species numbers. No dependable pattern of species distribution was noted; i.e., all sites had the same species even if all species were not present at all times. The genera Actinella, Anomoeoneis, Betrachospermum, Eunotia, Fragilaria, Frustulia, Mougeotia, Navicula, Neidium, Nitzschia, Peronia, Pinnularia, and Tabellaria were present in all or most all collections (Tables 3 and 4). Eunotia species were found in the greatest numbers (species and individuals). Twenty-three species of Eunotia were identified and verified by comparison with type specimens in the Herbarium of the Academy of Natural Sciences in Philadelphia (Table 2). Twenty-three species of Eunotia which could not be identified also were recorded. Most of these probably are new species which have not yet been described. Pinnularia was represented by 15 species, but most other genera were represented by only a few species.

Algae isolated from Rocky Creek, Turkey Creek, Site 64-1 and Site 64-2 are shown in Tables 3 and 4, respectively. Of these isolates, Monodus acuminata, Myrmecia, Nitzschia palea, Ankistrodesmus, Chlorella, and Selenastrum were not identified from the collections after microscopic examination.

4. MOBILITY OF DEPLETED URANIUM BY DISSOLUTION IN NATURAL WATERS ON RANGE C-74

An attempt to quantitatively estimate the amount of depleted uranium removed or mobilized by natural waters is discussed in Appendix A.

SECTION III

LABORATORY TESTS

1. MATERIALS AND METHODS

The oxides of uranium used in this investigation were U_3O_8 and UO_2, both in powdered form.

a. Algal Growth in Uranium-Containing Medium

The culture medium used depended upon the organism being tested. Green algae were grown in Bristol's Inorganic Mineral Solution (Deason and Bold, 1960). Diatoms were cultured in a modified FW-1 medium (Lewin, 1966) prepared without glycylglycine, but adjusted to an initial pH of 6.6 to 6.7. Biotin [1.0 milligrams per liter (mg/l)] was also included in this medium in addition to the other vitamins. The blue-green algal medium consisted of FW-1 further modified by reducing the concentration of $NaHCO_3$ and $Na_2SiO_3 \cdot H_2O$ each to 1.0 mg/l.

All cultures were maintained in 300-ml sidearm flasks containing 50 ml of medium. Inoculation was by sterile pipette and consisted of 1.0 ml of medium from an axenic liquid culture. Flasks were maintained at a temperature of 20 ± 1°C. Illumination was by cool-white fluorescent tubes at an intensity of 300 footcandles (fc).

Growth determinations were made by turbidimetric readings using a Klett-Summerson Colorimeter with a red filter. Readings were made at regular intervals during the logarithmic growth phase of the controls (no uranium) with the final reading taken approximately 7 to 14 days after inoculation.

Testing for algal growth inhibition consisted of two stages.

Stage 1: U_3O_8 or UO_2 in powdered form was added to the medium suitable for the alga being tested. Concentrations of uranium salt (0.1 percent by weight) were such that a saturated solution was maintained throughout the growth period. At the end of the experiment a t-test (Sokal and Rohlf, 1969) was used to compare the amount of growth in the presence of uranium with that of controls containing no uranium. If the outcome indicated growth inhibition was statistically significant (5 percent level) then Stage 2 was initiated.

Stage 2: 10.0 milligrams (mg) of solid U_3O_8 or UO_2 were added to a suitable medium and allowed to stir for 28 to 30 days, after which any undissolved uranium was removed by filtering. Samples of the filtered media were sent to Los Alamos Scientific Laboratory for analysis of the uranium content of the saturated medium. The levels of saturation were found to vary according to the medium used.

Growth inhibiting properties of the media were tested by inoculating algae into mixtures of uranium-containing medium and control (no uranium) medium such that the range of dilution was 100-, 80-, 60-, 40-, 30-, and 0-percent uranium-saturated medium. Statistical comparison of the results indicated which dilutions produced significant growth inhibition. This information, in addition to the results of the Los Alamos Scientific Laboratory analyses, provided a quantitative measure of the levels of uranium producing inhibitory effects.

b. Uranium Uptake, First Replicate

The procedure used for this experiment was as follows: Cells of the alga to be tested were cultured in medium lacking uranium, then harvested by centrifugation, and diluted with 20.0 ml of 1.01 M PO_4 buffer (pH 7.0). Five 4.0-ml aliquots of the cell suspension (each with 0.6-gm cells) were subjected to the following treatments, respectively.

(1A) Aliquot 1 was placed in 25.0 ml of Bristol's medium saturated with 6.9 parts per billion (ppb) dissolved U_3O_8. The sample was then placed in darkness for 12.0 hours at 0°C, after which the cells were harvested by centrifugation.

(1B) Aliquot 2 was placed in 25.0 ml of medium saturated with 2.9 ppb dissolved U_3O_8. The sample was then illuminated with cool-white fluorescent tubes at an intensity of 300 fc with 1 percent CO_2 in air bubbled through the medium. After 12.0 hours at 20°C, the cells were harvested by centrifugation.

(2A) Aliquot 3 was placed in 25.0 ml of medium saturated with 3.2 ppb dissolved UO_2. The sample was then placed in darkness for 12.0 hours at 0°C, after which the cells were harvested by centrifugation.

(2B) Aliquot 4 was placed in 25.0 ml of medium saturated with 3.2 ppb dissolved UO_2. The sample was then illuminated with cool-white fluorescent tubes at an intensity of 300 fc with 10 percent CO_2 in air bubbled through the medium. After 12.0 hours at 20°C the cells were harvested by centrifugation.

(3) Aliquot 5 (control) was harvested immediately by centrifugation.

All harvested samples were brought to a final volume of 100.0 ml with distilled water plus 1.0 ml concentrated HNO_3 before being sent to Los Alamos Scientific Laboratory for uranium assay.

The following protocol was used to determine an accumulation factor for the purpose of comparing the initial amount of uranium in each sample with the final amount present in the harvested cells.

(1) The amount of uranium present in each sample was calculated in the following manner, assuming a diffusion equilibrium existed between the medium and the cells.

$$\frac{\text{volume of uranium saturated medium}}{\text{total volume of uranium saturated medium plus cells}} \times \text{concentration of uranium in the saturated medium} = \text{initial concentration of uranium [microgram/liter } (\mu g/l)] \text{ in each sample}$$

(2) The amount of uranium present in each 100.0-ml sample was determined by assay. The amount present in the harvested cells was calculated in the following manner:

$$\frac{\text{volume of assayed sample}}{\text{volume of cells/sample}} \times \frac{\text{concentration of uranium/}}{\text{sample}} = \text{final concentration of uranium } (\mu g/l) \text{ on cells}$$

(3) The accumulation factor for each treatment was calculated using the results of (1) and (2).

$$\frac{\text{final concentration of uranium in cells}}{\text{initial concentration of uranium in sample}} = \text{Accumulation Factor}$$

c. Uranium Uptake, Second Replicate

The procedure followed was identical to that followed in the first replicate, except that two additional treatments were included. In one treatment there was a 5-minute exposure of the cells to U_3O_8; in the other there was a 5-minute exposure of cells to UO_2.

2. RESULTS

a. Algal Growth in Uranium-Containing Medium

Eight strains of algae were isolated from Rocky and Turkey Creeks and tested for growth inhibition in the presence of uranium. All species are listed in Table 5 and will henceforth be referred to by their designated code numbers.

Four green algal isolates (AF 42, 3, 12, and 37) were subjected to Stage 1 tests, the results of which are shown in Tables 6 through 13. According to the statistical analyses, only isolate AF 37 was significantly inhibited by both solid uranium oxides in the medium. Stage 2 tests were conducted on this isolate using two stock solutions of Bristol's medium, one of which was indicated to be saturated with 6.9 ppb dissolved U_3O_8, while the other contained 3.2 ppb dissolved UO_2 (saturated). The results of the Stage 2 tests (Tables 14 and 15) indicate that U_3O_8 inhibits the growth of AF 37 at levels of 6.3 ppb and higher ($\geq$ 60 percent U_3O_8 saturated medium). Growth of this organism is also reduced by UO_2, with concentrations of 2.6 ppb and higher ($\geq$ 80 percent UO_2 saturated medium) producing significant inhibition.

Both diatom isolates (AF 75 and 86) were found to be sensitive to excesses of solid U_3O_8 and UO_2 (Tables 16 through 19). However, since AF 75 and 86 are different isolates of the same species, and since both behaved identically in the Stage 1 procedure, further growth tests were conducted only on AF 75. Stage 2 tests with this isolate utilized FW-1 medium 2.0 ppb UO_2. Attempts to saturate this medium with U_3O_8 and remove dissolved uranium oxide apparently were unsuccessful, in that Los Alamos Scientific Laboratory analyses of uranium present indicated values of about 900 ppb, which is relatively high. Growth of the diatoms was significantly reduced by UO_2 (Table 20), but only at concentrations equal to 100 percent UO_2 saturated medium.

Both blue-green algal isolates (AF 219 and 214) were found to be inhibited in Stage 1 tests with solid U_3O_8 (Tables 21 and 22). However, a comparison of similar tests (Tables 23 and 24, respectively) showed that only AF 214 was sensitive to solid UO_2. Stage 2 tests were performed on AF 214 using FW-1 medium with 2.0 ppb dissolved UO_2. The medium saturated with UO_2, 2.0 ppb, inhibited growth of AF 214, but concentrations of 1.6 ppb or lower did not (Table 25). A summary of the results of the Stage 2 growth tests is shown in Table 26.

b. Uranium Accumulation

Results of the experiments dealing with uranium uptake are shown in Tables 27 and 28. The uranium accumulation patterns are similar in the two replicates in that there was more accumulation in light at 20°C than in darkness at 0°C. However, the accumulation factors in the second replicate were significantly higher than those in the first.

SECTION IV

DISCUSSION AND CONCLUSIONS

The diversity of algal species in Eglin streams indicates good water quality. The differences in species numbers in Rocky Creek (near a depleted uranium firing range) and Turkey Creek (control) probably are due to the shading of the Turkey Creek collection site. No significant seasonal differences in species numbers at any of the sites were noted, although the same species were not always present. Seasonal growth of individual species probably occurred. There was no evidence that uranium in the streams had any influence on the algal populations during the study period.

Limited analytical and empirical evidence indicates that waters associated with Range C-74 should have a usual pH range of 4.6 to 7, an oxidation potential (Eh) of 0.7 to 0.0 volt (V), and contain limited quantities of dissolved constituents. In this pH range and when the Eh is near zero, depleted uranium metal in the penetrators will react with and hydrolize water to form uranus hydroxide complexes. The complexes will move with the water flow into surrounding areas and be precipitated as uraninite (UO_2) or as amorphous UO_2. Under more oxidizing conditions uranium is mobilized as uranyl complexes (UO_2^{2+} and $UO_2CO_3^0$) and will be fixed by sorption on ferric oxyhydroxide compounds or precipitated as carnotite if sufficient potassium and vanadium are present. In either case the concentration of uranium in water escaping Range C-74 (neglecting overland flow) should be in the low part-per-billion range.

Results of the laboratory experiments show that the individual isolates exhibited varying levels of sensitivity to uranium. In general, the growth response of the isolates is in accord with a previous study in which terrestrial plants were observed to show differential sensitivity to uranium ore deposits (Cannon, 1952). Of the eight isolates tested, the most dramatic reduction in growth was seen in the diatoms. A similar effect was observed in an earlier study in which uranium concentrations exceeding 100 parts per billion were reported to severely reduce diatom survival (Hansen, 1974).

The studies on uranium uptake indicate that algal cells can accumulate uranium to concentrations higher by several orders of magnitude than the uranium in solution. The relatively small differences between treatment accumulation factors within each replicate (Tables 27 and 28) would seem to indicate uranium uptake by AF 37 is primarily due to physical adsorption on the cell surface rather than uptake mediated by metabolic processes. A similar finding has been previously reported for Chlorella regularis (Sakaguchi, Horikoshi, and Nakajima, 1978). In addition, uranium uptake associated with the formation of physiologically inactive complexes has been observed in several organisms including bacteria, yeast, marine algae, and sponges.

Specifically, the adsorption of the two uranium oxides by isolate AF 37 indicates the presence of numerous binding sites on the cell wall and/or membrane. The fact that the light-treated cells accumulated more uranium than those placed in darkness can probably be attributed to metabolic activity which increased growth, thereby producing additional binding sites. Previously, Rothstein and Meier (1951) and Tuovinen and Kelly (1973a) reported that uranium inhibited cell metabolism in bacteria and yeast by competing with essential ions for binding sites on the cell surface. The levels of uptake observed for this experiment indicate a similar competition may exist between the uranium oxides and components of the algal growth media. If this is true, the rate of metabolism in the uranium sensitive isolates may have been reduced, thereby resulting in the observed levels of growth inhibition.

The laboratory conditions for these growth and uptake studies were very different from natural conditions in the streams that were studied. Algae in the standing cultures were continuously exposed to uranium. Doctor Hughes' conclusion is that the uranium concentration in water escaping from Range C-74 would not exceed the low-ppb-range. In the running water of the streams the disolved uranium would be significantly lower than this for two reasons: (1) Only a part of the watershed contains any depleted uranium, and (2) Most of the water ultimately reaching the streams moves past any contaminating uranium too fast to become uranium saturated. Therefore, it is highly unlikely that even the most sensitive species, such as the diatoms, are being inhibited by depleted uranium coming from Range C-74.

The capacity of the algae to accumulate uranium, either by physical adsorption or metabolic processes, will have little effect, if any, upon the ecology of the area.

TABLE 1. Physical Properties of Water From Turkey and Rocky Creeks During 1977.

Date	Rocky Creek	Turkey Creek
24/2/77	pH 5.3	5.4
	DO 8.2 ppm	8.2
	Temp. 17.0°C	20.0°C
4/5/77	pH 5.2	5.3
	DO 9.4 ppm	7.6 ppm
	Temp. 17.0°C	20.0°C
2/6/77	pH 5.3	5.2
	DO 8.4 ppm	9.0 ppm
	Temp 20.0°C	21.0°C
28/6/77	pH 5.3	5.2
	DO 7.4 ppm	7.0 ppm
	Temp. 22.0°C	23.0°C

TABLE 2. Physical Properties of Water From Sites 64-1 and 64-2 During 1979.

Date	Site 64-1	Site 64-2
16/2/79	Not available	Not available
2/4/79	pH 5.1 DO 8.0 ppm Temp. 20.0°C	4.9 8.0 ppm 20.0°C
1/5/79	pH 4.9 DO 8.4 ppm Temp. 18.0°C	4.9 8.4 ppm 18.0°C
21/5/79	pH 4.9 DO 8.4 ppm Temp. 19.0°C	4.9 8.6 ppm 20.0°C
18/6/79	pH 5.2 DO 8.0 ppm Temp 21.0°C	5.0 8.4 ppm 20.0°C
2/8/79	Not available	Not available
22/8/79	pH 5.2 DO 8.2 ppm Temp. 21.0°C	5.2 7.8 ppm 21.0°C

TABLE 3. Algal Genera and Species Exclusive of Diatoms.

Collection Site and Date	Rocky Creek 24/2/77	Turkey Creek 24/2/77	Rocky Creek 4/5/77	Turkey Creek 4/5/77	Rocky Creek 2/6/77	Turkey Creek 2/6/77	Rocky Creek 28/6/77	Turkey Creek 28/6/77	Site 64-1 16/2/79	Site 64-2 16/2/79	Site 64-1 2/4/79	Site 64-2 2/4/79	Site 64-1 1/5/79	Site 64-2 1/5/79
Actinotaenium sp.					X									
Ammatoidea sp.					X		X				X		X	X
Anabaena sp.					X		X	X					X	
Anacystis sp.								X						
Betrachospermum sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Binucleria sp.	X		X		X		X							
Bulbochaete sp.							X						X	X
Calothrix sp.											X	X		
Chaetosphaeridium sp.														
Chlamydomonas sp.					X	X	X		X					
Chromulina sp.					X									
Chrysococcus sp.					X									
Chrysophytan flagellate							X	X				X	X	X
Chrysopyxis sp.														
Closterium sp.	X				X									
Coccoid green										X		X		
Cosmarium sp.	X				X	X	X				X		X	X
Cryptomonas sp.							X		X				X	X
Cylindrocystis sp.									X		X	X		X
Cylindrospermum sp.														

TABLE 3. Algal Genera and Species Exclusive of Diatoms. (Continued)

Collection Site and Date	Rocky Creek 24/2/77	Turkey Creek 24/2/77	Rocky Creek 4/5/77	Turkey Creek 4/5/77	Rocky Creek 2/6/77	Turkey Creek 2/6/77	Rocky Creek 28/6/77	Turkey Creek 28/6/77	Site 64-1 16/2/79	Site 64-2 16/2/79	Site 64-1 2/4/79	Site 64-2 2/4/79	Site 64-1 1/5/79	Site 64-2 1/5/79
Dicranochaete sp.														
Dinoflagellate sp.								X						X
Euastrum sp.	X													
Euglena sp.	X						X					X		
Euglenoid flagellate								X						
Gloeocystis sp.											X			
Gonatozygon sp.														
Gymnodinium sp.						X								
Hyalotheca sp.											X			X
Lyngyba sp.			X											
Mallomonas sp.									X					
Merismopedia sp.	X													
Microspora sp.	X				X						X	X		
Microsterias sp.	X													
Mougeotia sp.	X	X	X		X		X		X		X	X	X	X
Netrium digitas sp.	X		X		X	X	X						X	X
Oedogonium sp.					X		X							
Oscillatoria sp.	X				X		X							
Penium sp.					X	X	X						X	X
Peridinium sp.					X									X

TABLE 3. Algal Genera and Species Exclusive of Diatoms. (Continued)

Collection Site and Date	Rocky Creek 24/2/77	Turkey Creek 24/2/77	Rocky Creek 4/5/77	Turkey Creek 4/5/77	Rocky Creek 2/6/77	Turkey Creek 2/6/77	Rocky Creek 28/6/77	Turkey Creek 28/6/77	Site 64-1 16/2/79	Site 64-2 16/2/79	Site 64-1 2/4/79	Site 64-2 2/4/79	Site 64-1 1/5/79	Site 64-2 1/5/79
Plectonema sp.														
Pleurotaenium sp.	X										X			
Porphyrosiphon sp.									X		X		X	X
Scenedesmus sp.		X												
Scytonema sp.									X					
Spirogyra sp.	X				X		X							
Staurastrum sp.					X						X			X
Stichococcus sp.														
Synura sp.	X						X				X			
Tetmemorus sp.													X	X
Tolypothrix sp.													X	
Ulothrix sp.							X							
Zygnema sp.	X						X		X					

TABLE 3. Algal Genera and Species Exclusive of Diatoms. (Continued)

Collection Site & Date	Site 64-1 21/5/79	Site 64-2 21/5/79	Site 64-1 18/6/79	Site 64-2 18/6/79	Site 64-1 2/8/79	Site 64-2 2/8/79	Site 64-1 22/8/79	Site 64-2 22/8/79
Actinotaenium sp.								
Ammatoidea sp.					X		X	X
Anabaena sp.	X				X			
Anacystis sp.								
Betrachospermum sp.	X	X	X	X	X	X	X	X
Binucleria sp.							X	X
Bulbochaete sp.	X							X
Calothrix sp.		X						
Chaetosphaeridium sp.								X
Chlamydomonas sp.	X	X					X	X
Chromulina sp.								
Chrysococcus sp.								
Chrysophytan flagellate						X	X	
Chrysopyxis sp.								
Closterium sp.		X		X		X		
Coccoid green	X				X	X	X	X
Cosmarium sp.			X	X			X	X
Cryptomonas sp.						X		X
Cylindrocystis sp.		X	X		X		X	X
Cylindrospermum sp.			X					

TABLE 3. Algal Genera and Species Exclusive of Diatoms. (Continued)

Collection Site and Date	Site 64-1 21/5/79	Site 64-2 21/5/79	Site 64-1 18/6/79	Site 64-2 18/6/79	Site 64-1 2/8/79	Site 64-2 2/8/79	Site 64-1 22/8/79	Site 64-2 22/8/79
Dicranochaete sp.								X
Dinoflagellate sp.		X			X			X
Euastrum sp.		X						X
Euglena sp.								
Euglenoid flagellate					X			X
Gloeocystis sp.								
Gonatozygon sp.			X					
Gymnodinium sp.	X							
Hyalotheca sp.					X			
Lyngyba sp.								
Mallomonas sp.								
Merismopedia sp.		X						
Microspora sp.								
Microsterias sp.								
Mougeotia sp.	X	X	X	X	X	X	X	X
Netrium digitas sp.	X						X	X
Oedogonium sp.								X
Oscillatoria sp.	X	X				X	X	
Penium sp.	X	X		X				
Peridinium sp.								

TABLE 3. Algal Genera and Species Exclusive of Diatoms. (Concluded)

Collection Site and Date	Site 64-1 21/5/79	Site 64-2 21/5/79	Site 64-1 18/6/79	Site 64-2 18/6/79	Site 64-1 2/8/79	Site 64-2 2/8/79	Site 64-1 22/8/79	Site 64-2 22/8/79
Plectonema sp.			X					
Pleurotaenium sp.		X		X				X
Porphyrosiphon sp.			X		X		X	
Scenedesmus sp.								
Scytonema sp.								
Spirogyra sp.	X						X	
Staurastrum sp.	X	X	X				X	
Stichococcus sp.								X
Synura sp.	X			X				
Tetmemorus sp.		X			X			
Tolypothrix sp.							X	
Ulothrix sp.								X
Zygnema sp.								

TABLE 4. Bacillariophyceae (Diatoms)

Collection Site and Date	Rocky Creek 24/2/77	Turkey Creek 24/2/77	Rocky Creek 6/5/77	Turkey Creek 6/5/77	Rocky Creek 2/6/77	Turkey Creek 2/6/77	Rocky Creek 28/6/77	Turkey Creek 28/6/77	Site 64-1 15/2/79	Site 64-2 15/2/79	Site 64-1 2/4/79	Site 64-2 2/4/79	Site 64-1 1/5/79	Site 64-2 1/5/79	Site 64-1 21/5/79	Site 64-2 21/5/79
Actinella punctata Lewis var. punctata Patr. et Reim.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Anomoeoneis follis (Ehr.) Cl. var. follis Patr. et Reim.	X		X		X		X			X		X				X
A. serians var. apiculata Boyer										X	X			X	X	X
A. serians var. brachysira (Breb. ex Kutz.) Hust.	X	X	X	X		X	X	X	X		X	X	X	X	X	X
A. serians (Breb ex Kutz.) var. serians Patr. et Reim.					X				X	X	X	X	X		X	X
A. vitrea (Grün) Ross var. vitrea Patr. et Reim.					X											
Asterionella formosa Hass. var. formosa Patr. et Reim.									X							
Achnanthes gibberula Grün. var. gibberula Patr. et Reim.		X														
Cocconeis sp.	X															
Cyclotella stelligera Cl. et Grün.		X														
Cyclotella comta (Ehr.) Kutz.																X
Cymbella brehmii Hust. var. brehmii Patr. et Reim.												X				
Cymbella minuta var. gracilis (Cholon.) Reim.		X			X											
Cymbella sp.						X	X	X								
Epithemia sp.	X															

TABLE 4. Bacillariophyceae (Diatoms) (Continued)

Collection Site and Date	Rocky Creek 24/2/77	Turkey Creek 24/2/77	Rocky Creek 6/5/77	Turkey Creek 6/5/77	Rocky Creek 2/6/77	Turkey Creek 2/6/77	Rocky Creek 28/6/77	Turkey Creek 28/6/77	Site 64-1 15/2/79	Site 64-2 15/2/79	Site 64-1 2/4/79	Site 64-2 2/4/79	Site 64-1 1/5/79	Site 64-2 1/5/79	Site 64-1 21/5/79	Site 64-2 21/5/79
Eunotia bidentula W. Sm. var. bidentula Patr. et Reim.	X	X	X	X		X	X		X	X	X	X	X	X	X	X
E. carolina Patr. var. carolina Patr. et Reim.		X	X	X			X	X		X	X	X	X	X	X	X
E. curvata (Kütz.) Lagerst. var. curvata Patr. et Reim.	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X
E. denticulata (Breb.) Rabh.										X		X				
E. diodon Ehr. var. diodon Patr. et Reim.			X	X											X	
E. elegans oster. var. elegans Patr. et Reim.	X	X					X									
E. exgracilis (W. Sm. em.) A. Berg in Cleve-Eul.										X	X	X				
E. exigua (Breb ex Kütz) Rabh.																
E. flexuosa Breb. ex Kütz. var. flexuosa Patr. et Reim.	X								X	X	X	X	X	X	X	X
E. hexaglyphis Ehr.		X				X	X			X			X		X	X
E. incisa W. Sm. ex Greg.			X	X				X		X						
E. koeheliensis O. Mull.																
E. maior (W. Sm.) Rabh. var. maior Patr. et Reim.			X							X		X		X		X
E. monodon var. constricta Cl.-Eul.	X	X	X	X	X	X	X	X	X	X	X		X	X	X	X
E. monodon Ehr. var. monodon Patr. et Reim.				X				X	X				X	X		X

TABLE 4. Bacillariophyceae (Diatoms) (Continued)

Collection Site and Date	Rocky Creek 24/2/77	Turkey Creek 24/2/77	Rocky Creek 6/5/77	Turkey Creek 6/5/77	Rocky Creek 2/6/77	Turkey Creek 2/6/77	Rocky Creek 28/6/77	Turkey Creek 28/6/77	Site 64-1 15/2/79	Site 64-2 15/2/79	Site 64-1 2/4/79	Site 64-2 2/4/79	Site 64-1 1/5/79	Site 64-2 1/5/79	Site 64-1 21/5/79	Site 64-2 21/5/79
Eunotia Naegelii migula var. Naegelii Patr. et Reim.	X								X	X	X	X	X	X	X	X
E. nymanniana Grun. var. nymanniana Patr. et Reim.	X		X		X		X	X		X	X	X	X		X	
E. obesa var. wardii Patr.									X	X	X	X	X	X	X	X
E. Parallela Ehr. var. Parallela Patr. et Reim.		X	X													
E. pectinalis (O.F. Mull.?) Rabh.						X					X	X			X	
E. praerupta Ehr.			X							X	X					
E. sudetica O. Mull. var. sudetica Patr. et Reim.	X	X	X	X	X	X	X	X	X	X	X	X		X	X	
E. vanheurckii var. intermedia (Krasske ex Hust.) Patr.											X	X		X	X	X
E. vanheurckii Patr. var. vanheurckii Patr. et Reim.	X	X	X	X		X	X	X	X			X	X	X		
E. zygodon Ehr. var. zygodon Patr. et Reim.	X	X		X		X	X	X	X	X	X	X	X	X	X	X
Fragilaria construens (Ehr.) Grun.			X				X	X	X	X		X	X		X	X
Fragilaria *crotonensis* Kitton var. crotonensis Reim. Patr. et Reim.							X									
F. pinnata Ehr.																
F. strangulans Zanon		X	X		X		X	X								

TABLE 4. Bacillariophyceae (Diatoms) (Continued)

Collection Site and Date	Rocky Creek 24/2/77	Turkey Creek 24/2/77	Rocky Creek 6/5/77	Turkey Creek 6/5/77	Rocky Creek 2/6/77	Turkey Creek 2/6/77	Rocky Creek 28/6/77	Turkey Creek 28/6/77	Site 64-1 15/2/79	Site 64-2 15/2/79	Site 64-1 2/4/79	Site 64-2 2/4/79	Site 64-1 1/5/79	Site 64-2 1/5/79	Site 64-1 21/5/79	Site 64-2 21/5/79
Fragilaria virescens Ralfs var. virescens Patr. et Reim.					X			X								
Frustulia rhomboides var. capitata (A. Mayer) Patr. comb. nov.		X	X	X	X	X	X	X		X		X	X		X	X
F. rhomboides (Ehr.) DeT. var. rhomboides Patr. et Reim.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
F. vulgaris (Twaites) DeT. var. vulgaris Patr. et Reim. ?									X							
Gomphonema lagerheimi A. Cl.		X							X		X	X	X		X	X
Gomphonema turria Ehr. var. turria		X														
Gomphonema gracile Ehr. emend V.H. var.. gracile Patr. et Reim.							X									
Gomphonema parvulum (Kütz.) var. parvulum Patr. et. Reim.		X	X													
Hantzschia amphioxys (Ehr.) Grun.												X				
Melosira sp.	X															
Navicula angusta O. Mull.	X								X	X			X			
N. confervacea var. perigrina (W. Sm.) Grun. ?									X							
N. mutica Kütz. ?																
N. savannahiana Patr. var. savannahiana Patr. et Reim.		X														

TABLE 4. Bacillariophyceae (Diatoms) (Continued)

Collection Site and Date	Rocky Creek 24/2/77	Turkey Creek 24/2/77	Rocky Creek 6/5/77	Turkey Creek 6/5/77	Rocky Creek 2/6/77	Turkey Creek 2/6/77	Rocky Creek 28/6/77	Turkey Creek 28/6/77	Site 64-1 15/2/79	Site 64-2 15/2/79	Site 64-1 2/4/79	Site 64-2 2/4/79	Site 64-1 1/5/79	Site 64-2 1/5/79	Site 64-1 21/5/79	Site 64-2 21/5/79
Navicula affine (Ehr.) Pfitz var. affine Patr. et Reim.	X		X	X	X		X									
N. apiculatum Reim. var. apiculatum Patr. et Reim.				X			X				X	X		X		
Neidium bisulcatum (Lagerst.) Cl. var. bisulcatum Patr. et Reim.																
N. iridis var. amphigomphus (Ehr.) A. Mayer	X		X				X		X				X	X		
N. tumescens (Grun.) Cl. var. tumescens Patr. et Reim.	X						X									
Nitzschia lorenziana Grun. var. subtilis Grun.	X				X		X			X			X			
N. subacicularis Hust.	X										X		X	X		
Peronia fibula (Breb. ex Kütz.) Ross var. fibula Patr. et Reim.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Pinnularia abaujensis (Pant.) Ross var. abaujensis Patr. et Reim.						X					X	X	X			
P. acuminata W. Sm. var. acuminata Patr. et Reim.										X						
P. biceps Greg. var. biceps Patr. et Reim.				X		X						X				
P. dactylus Greg. var. ?																X
P. legumen (Ehr.) Ehr. var. legumen Patr. et Reim.			X		X		X									
P. mesogongyla Ehr. var. mesogongyla Patr. et Reim.		X														

TABLE 4. Bacillariophyceae (Diatoms) (Continued)

Collection Site and Date	Rocky Creek 24/2/77	Turkey Creek 24/2/77	Rocky Creek 6/5/77	Turkey Creek 6/5/77	Rocky Creek 2/6/77	Turkey Creek 2/6/77	Rocky Creek 28/6/77	Turkey Creek 28/6/77	Site 64-1 15/2/79	Site 64-2 15/2/79	Site 64-1 2/4/79	Site 64-2 2/4/79	Site 64-1 1/5/79	Site 64-2 1/5/79	Site 64-1 21/5/79	Site 64-2 21/5/79
Pinnularia mesolepta (Ehr.) W. Sm. var. mesolepta Patr. et Reim.	X				X		X			X				X		
P. nodosa (Ehr.) W. Sm. var. modosa Patr. et Reim.									X			X				X
P. obscura Krasske		X							X		X					
P. ruttneri Hust. var. ruttneri Patr. et Reim.						X										
P. socialis (T. C. Palm) Hust. var. socialis Patr. et Reim.		X	X			X										
P. subcapitata Greg. var. subcapitata Patr. et Reim.			X	X		X				X						
P. substromatophora Hust. var. substromatophora Patr. et Reim.		X														
P. sudetica Hilse var. sudetica Patr. et Reim.	X		X	X				X	X	X	X	X	X	X	X	X
Stauroneis anceps f. linearis (Ehr.)Hust.	X					X										
Stenopterobia intermedia (Lewis) Fricke	X											X				
Surirella baileyii Lewis												X				
Surirella elegans Ehr.			X													
S. sp.	X				X		X	X								
Synedra rumpens var. familiaris (Kütz.) Hust.		X														

TABLE 4. Bacillariophyceae (Diatoms) (Continued)

Collection Site and Date	Rocky Creek 24/2/77	Turkey Creek 24/2/77	Rocky Creek 6/5/77	Turkey Creek 6/5/77	Rocky Creek 2/6/77	Turkey Creek 2/6/77	Rocky Creek 28/6/77	Turkey Creek 28/6/77	Site 64-1 15/2/79	Site 64-2 15/2/79	Site 64-1 2/4/79	Site 64-2 2/4/79	Site 64-1 1/5/79	Site 64-2 1/5/79	Site 64-1 21/5/79	Site 64-2 21/5/79
Synedra ulna var. danica (Kütz.) V.H.		X														
Tabellaria binalis (Ehr.?) Grun. var. binalis Patr. et Reim.			X		X		X		X			X				
T. flocculosa (Roth) Kütz. var. flocculosa Patr. et Reim.	X		X	X	X		X		X	X	X	X	X	X	X	X

TABLE 4. Bacillariophyceae (Diatoms) (Continued)

Collection Site and Date	Site 64-1 18/6/79	Site 64-2 18/6/79	Site 64-1 2/8/79	Site 64-2 2/8/79	Site 64-1 22/8/79	Site 64-2 22/8/79
Actinella punctata Lewis var. punctata Patr. et Reim.	X	X	X	X	X	X
Anomoeoneis follis (Ehr.) Cl. var. follis Patr. et Reim.		X				X
A. serians var. apiculata Boyer		X	X	X	X	X
A. serians var. brachysira (Breb. ex Kutz.) Hust.	X	X	X	X	X	X
A. serians (Breb ex Kutz.) var. serians Patr. et Reim.	X	X	X	X	X	X
A. vitrea (Grün) Ross var. vitrea Patr. et Reim.						
Asterionella formosa Hass. var. formosa Patr. et Reim.			X	X		X
Achnanthes gibberula Grün. var. gibberula Patr. et Reim.						
Cocconeis sp.						
Cyclotella stilligura Cl. et Grün.						
Cyclotella comta (Ehr.) Kutz.	X					
Cymbella brehmii Hust. var. brehmii Patr. et Reim.		X				
Cymbella minuta var. gracilis (Cholon.) Reim.						
Cymbella sp.	X					
Epithemia sp.						

TABLE 4. Bacillariophyceae (Diatoms) (Continued)

Collection Site and Date	Site 64-1 18/6/79	Site 64-2 18/6/79	Site 64-1 2/8/79	Site 64-2 2/8/79	Site 64-1 22/8/79	Site 64-2 22/8/79
Eunotia bidentula W. Sm. var. bidentula Patr. et Reim.	X	X	X	X	X	X
E. carolina Patr. var. carolina Patr. et Reim.	X				X	X
E. curvata (Kützt.) Lagerst. var. curvata Patr. et Reim.		X	X		X	X
E. denticulata (Breb.) Rabh.		X	X	X	X	X
E. diodon Ehr. var. diodon Patr. et Reim.		X?				
E. elegans oster. var. elegans Patr. et Reim.						
E. exgracilis (W. Sm. em.) A. Berg in Cleve-Eul.	X	X				X
E. exigua (Breb ex Kütz) Rabh.						
E. flexuosa Breb. ex Kütz. var. flexuosa Patr. et Reim.	X	X	X	X	X	X
E. hexaglyphis Ehr.						
E. incisa W. Sm. ex Greg.						X
E. koeheliensis O. Mull.	X		X			
E. maior (W. Sm.) Rabh. var. maior Patr. et Reim.		X	X	X	X	X
E. monodon var. constricta C.-Eul.	X	X	X	X	X	X
E. monodon Ehr. var. monodon Patr. et Reim.	X	X		X	X	X

TABLE 4. Bacillariophyceae (Diatoms) (Continued)

Collection Site and Date	Site 64-1 18/6/79	Site 64-2 18/6/79	Site 64-1 2/8/79	Site 64-2 2/8/79	Site 64-1 22/8/79	Site 64-2 22/8/79
Eunotia Naegelii migula var. Naegelii Patr. et Reim.		X	X	X	X	X
E. nymanniana Grun. var. nymanniana Patr. et Reim.	X	X	X	X	X	
E. obesa var. wardii Patr.	X	X	X	X	X	X
E. Parallela Ehr. var. Parallela Patr. et Reim.						
E. pectinalis (O.F. Mull.?) Rabh.						
E. praerupta Ehr.						
E. sudetica O. Mull. var. sudetica Patr. et Reim.	X	X	X		X	X
E. vanheurckii var. intermedia (Krasske ex Hust.) Patr.	X				X	X
E. vanheurckii Patr. var. vanheurckii Patr. et Reim.						
E. zygodon Ehr. var. zygodon Patr. et Reim.	X	X	X	X	X	X
Fragilaria construens (Ehr.) Grun.	X	X	X	X	X	X
Fragilaria construens Kitton var. crotonensis Reim. Patr. et Reim.						
F. pinnata Ehr.						
F. strangulans Zanon	X					

TABLE 4. Bacillariophyceae (Diatoms) (Continued)

Collection Site and Date	Site 64-1 18/6/79	Site 64-2 18/6/79	Site 64-1 2/8/79	Site 64-2 2/8/79	Site 64-1 22/8/79	Site 64-2 22/8/79
Fragilaria virescens Ralfs var. virescens Patr. et Reim.						
Frustulia rhomboides var. capitata (A. Mayer) Patr. comb. nov.	X	X	X	X	X	X
F. rhomboides (Ehr.) DeT. var. rhomboides Patr. et Reim.	X	X	X	X	X	X
F. vulgaris (Twaites) DeT. var. vulgaris Patr. et Reim. ?						
Gomphonema lagerheimi A. Cl.						
Gomphonema turria Ehr. var. turria						
Gomphonema gracile Ehr. emend V.H. var.. gracile Patr. et Reim.	X	X	X	X	X	X
Gomphonema parvulum (Kütz.) var. parvulum Patr. et. Reim.						
Hantzschia amphioxys (Ehr.) Grun.						
Melosira sp.						
Navicula angusta O. Mull.			X			X
N. confervacea var. perigrina (W. Sm.) Grun. ?						
N. mutica Kütz. ?	X					
N. savannahiana Patr. var. savannahiana Patr. et Reim.						

TABLE 4. Bacillariophyceae (Diatoms (Continued)

Collection Site and Date	Site 64-1 18/6/79	Site 64-2 18/6/79	Site 64-1 2/8/79	Site 64-2 2/8/79	Site 64-1 22/8/79	Site 64-2 22/8/79
Navicula affine (Ehr.) Pfitz var. affine Patr. et Reim.						
N. apiculatum Reim. var. apiculatum Patr. et Reim.	X	X				
Neidium bisulcatum (Lagerst.) Cl. var. bisulcatum Patr. et Reim.	X	X				
N. iridis var. amphigomphus (Ehr.) A. Mayer						X
N. tumescens (Grun.) Cl. var. tumescens Patr. et Reim.						X
Nitzschia lorenziana Grun. var. subtilis Grun.		X				X
N. subacicularis Hust.	X	X	X			X
Peronia fibula (Breb. ex KUtz.) Ross var. fibula Patr. et Reim.	X	X	X	X	X	X
Pinnularia abaujensis (Pant.) Ross var. abaujensis Patr. et Reim.						
P. acuminata W. Sm. var. acuminata Patr. et Reim.						
P. biceps Greg. var. biceps Patr. et Reim.	X					
P. dactylus Greg. var. ?	X		X	X		X
P. legumen (Ehr.) Ehr. var. legumen Patr. et Reim.						
P. mesogongyla Ehr. var. mesogongyla Patr. et Reim.						

TABLE 4. Bacillariophyceae (Diatoms) (Continued)

Collection Site and Date	Site 64-1 18/6/79	Site 64-2 18/6/79	Site 64-1 2/8/79	Site 64-2 2/8/79	Site 64-1 22/8/79	Site 64-2 22/8/79
Pinnularia mesolepta (Ehr.) W. Sm. Var. *mesolepta* Patr. et Reim.						
P. nodosa (Ehr.) W. Sm. var. *modosa* Patr. et Reim.						
P. obscura Krasske						
P. ruttneri Hust. var. *ruttneri* Patr. et Reim.						
P. socialis (T. C. Palm) Hust. var. *socialis* Patr. et Reim.						
P. subcapitata Greg. var. *subcapitata* Patr. et Reim.		X	X	X		X
P. substromatophora Hust. var. *substromatophora* Patr. et Reim.						
P. sudetica Hilse var. *sudetica* Patr. et Reim.	X	X	X	X	X	X
Stauroneis anceps f. *linearis* (Ehr.) Hust.					X	
Stenopterobia intermedia (Lewis) Fricke	X	X	X		X	X
Surirella baileyii Lewis	X	X	X		X	X
Surirella elegans Ehr.						
S. sp.						
Synedra rumpens var. *familiaris* (Kütz.) Hust.						

TABLE 4. Bacillariophyceae (Diatoms) (Concluded)

Collection Site and Date	Site 64-1 18/6/79	Site 64-2 18/6/79	Site 64-1 2/8/79	Site 64-2 2/8/79	Site 64-1 22/8/79	Site 64-2 22/8/79
Synedra ulna var. *danica* (Kütz.) V.H.						
Tabellaria binalis (Ehr.?) Grun. var. binalis Patr. et Reim.	X				X	X
T. flocculosa (Roth) Kütz. var. flocculosa Patr. et Reim.	X	X	X	X	X	X

TABLE 5. Algal Isolates from Rocky and Turkey Creeks.

CULTURE DESIGNATION	ALGAL DIVISION	ORGANISM
AF 3	Chlorophyta	*Monodus acuminata* Chodat
AF 37	Chlorophyta	*Monodus acuminata* Chodat
AF 42	Chlorophyta	*Chlorella* sp.
AF 12	Chlorophyta	*Myrmecia* sp.
AF 75	Chrysophyta	*Nitzschia palea*
AF 86	Chrysophyta	*Nitzschia palea*
AF 214	Cyanophyta	*Oscillatoria* sp.
AF 219	Cyanophyta	*Oscillatoria* sp.

TABLE 6. Algal Growth (turbidimetric Klett units) With and Without U_3O_8 (50 mg/50 ml culture medium); Organism is isolate AF 42 from Rocky Creek.

Flask #	x Control	y U_3O_8
1	84	96
2	78	62
3	85	70
4	79	65
5	89	89

$\bar{X} = 83.0$

$\bar{Y} = 76.4$

t = 0.93, not significant at the 5 percent level

TABLE 7. Algal Growth (turbidimetric Klett units) With and Without UO_2 (50 mg/50 ml culture medium); Organism is isolate AF 42 from Rocky Creek.

Flask #	x Control	y UO_2
1	84	71
2	78	67
3	85	54
4	79	89
5	89	72

$\bar{X} = 83.0$

$\bar{Y} = 70.6$

t = 2.08, not significant at the 5 percent level

TABLE 8. Algal Growth (turbidimetric Klett units) With and Without U_3O_8 (50 mg/50 ml culture medium); Organism is isolate AF 3 from Rocky Creek.

Flask #	x Control	y U_3O_8
1	89	278
2	94	131
3	190	111
4	120	264
5	194	158

$\bar{X}$ = 137.4

$\bar{Y}$ = 188.4

t = 1.229, not significant at the 5 percent level

TABLE 9. Algal Growth (turbidimetric Klett units) With and Without UO_2 (50 mg/50 ml culture medium); Organism is isolate AF 3 from Rocky Creek.

Flask #	x Control	y UO_2
1	89	85
2	94	97
3	190	164
4	120	95
5	194	191

$\bar{X} = 137.4$

$\bar{Y} = 126.4$

t = 0.35, not significant at the 5 percent level

TABLE 10. Algal Growth (turbidimetric Klett units) With and Without U_3O_8 (50 mg/50 ml culture medium); Organism is isolate AF 12 from Turkey Creek.

Flask #	x Control	y U_3O_8
1	131	226
2	218	191
3	220	158
4	178	150
5	224	197

$\bar{X} = 194.2$

$\bar{Y} = 184.4$

t = 0.43, not significant at the 5 percent level

TABLE 11. Algal Growth (turbidimetric Klett units) With and Without UO_2 (50 mg/50 ml culture medium); Organism is isolate AF 12 from Turkey Creek.

Flask #	x Control	y UO_2
1	131	219
2	218	204
3	220	184
4	178	219
5	224	192

$\bar{X} = 194.2$

$\bar{Y} = 203.6$

t = 0.48, not significant at the 5 percent level

TABLE 12. Algal growth (turbidimetric Klett units) With and Without U_3O_8 (50 mg/50 ml culture medium); Organism is isolate AF 37 from Rocky Creek.

Flask #	x Control	y U_3O_8
1	84	55
2	90	61
3	159	60
4	102	63
5	80	—

$\bar{X}$ = 103.0

$\bar{Y}$ = 59.8

t = 2.96, significant at the 5 percent level

TABLE 13. Algal Growth (turbidimetric Klett units) With and Without UO_2 (50 mg/50 ml culture medium); Organism is isolate AF 37 from Rocky Creek.

Flask #	x Control	y UO_2
1	84	73
2	90	45
3	159	73
4	102	42
5	80	86

$\bar{X}$ = 103.0

$\bar{Y}$ = 63.8

t = 2.32, significant at the 5 percent level

TABLE 14. Algal Growth (turbidimetric Klett units) With Dilutions of U_3O_8 Culture Medium; Organism is isolate AF 37 from Rocky Creek.

	Percent Saturated U_3O_8 Culture Medium					
Flask #	100%	80%	60%	40%	20%	0% (control)
1	68	65	68	96	56	98
2	86	60	82	68	105	78
3	85	62	86	86	104	101
4	67	70	65	63	66	101
5	82	102	76	92	110	108
mean	77.6	71.8	75.4	81.0	88.2	97.2
t	*2.98	*2.75	*3.38	1.95	0.73	

*t = Significant at the 5 percent level

TABLE 15. Algal Growth (turbidimetric Klett units) With Dilutions of UO_2 Culture Medium; Organism is isolate AF 37 from Rocky Creek.

	Percent Saturated U_3O_3 Culture Medium					
Flask #	100%	80%	60%	40%	20%	0% (control)
1	11	14	14	13	14	15
2	16	12	16	15	17	16
3	9	14	10	15	18	16
4	11	12	14	13	14	16
5	12	12	14	17	15	14
mean	11.8	12.8	13.6	14.6	15.6	15.4
t	*2.94	*4.11	1.7	0.94	0.22	

*t = Significant at the 5 percent level

TABLE 16. Algal Growth (turbidimetric Klett units) With and Without U_3O_8 (50 mg/50 ml culture medium); Organism is isolate AF 75 from Rocky Creek.

Flask #	x Control	y U_3O_8
1	37	22
2	36	18
3	24	25
4	26	13
5	30	14

$\bar{X} = 30.6$

$\bar{Y} = 18.4$

t = 3.52, significant at the 5 percent level

TABLE 17. Algal Growth (turbidimetric Klett units) With and Without UO_2 (50 mg/50 ml culture medium); Organism is isolate AF 75 from Rocky Creek.

Flask #	x Control	y UO_2
1	37	18
2	36	20
3	24	23
4	26	18
5	30	21

$\bar{X}$ = 30.6

$\bar{Y}$ = 20.0

t = 3.83, significant at the 5 percent level

TABLE 18. Algal Growth (turbidimetric Klett units) With and Without U_3O_8 in Culture Medium (50 µg/50 ml); Organism is isolate AF 86 from Rocky Creek.

Flask #	x Control	y U_3O_8
1	35	29
2	31	2
3	32	19
4	32	17
5	33	26

$\bar{X}$ = 32.6

$\bar{Y}$ = 18.6

t = 2.95, significant at the 5 percent level

TABLE 19. Algal Growth (turbidimetric Klett units) With and Without UO_2 (50 mg/50 ml culture medium); Organism is isolate AF 86 from Rocky Creek.

Flask #	x Control	y UO_2
1	35	19
2	31	22
3	32	24
4	32	24
5	33	21

$\bar{X}$ = 32.6

$\bar{Y}$ = 22.0

t = 9.09, significant at the 5 percent level

TABLE 20. Algal Growth (turbidimetric Klett units) With Dilutions of UO_2 in Culture Medium; Organism is isolate AF 75 from Rocky Creek.

	Percent Saturated UO_2 Culture Medium					
Flask #	100%	80%	60%	40%	20%	0%
1	31	46	48	46	44	45
2	27	52	66	56	45	30
3	21	49	41	66	47	56
4	25	59	45	49	50	52
5	30	48	52	40	44	43
mean	26.8	50.8	50.4	51.4	46.0	45.2
t	*3.82	1.12	0.84	0.98	0.17	

*t - Significant at the 5 percent level

TABLE 21. Algal Growth (turbidimetric Klett units) With and Without U_3O_8 (50 mg/50 ml culture medium); Organism is isolate AF 219 from Rocky Creek.

Flask #	x Control	y U_3O_8
1	11	5
2	18	4
3	23	15
4	31	14
5	30	6
6	16	4
7	20	10

$\bar{X} = 21.29$

$\bar{Y} = 8.29$

$t = 3.96$, significant at the 5 percent level

TABLE 22. Algal Growth (turbidimetric Klett units) With and Without U_3O_8 (50 mg/50 ml culture medium); Organism is isolate AF 214 from Rocky Creek.

Flask #	x Control	y U_3O_8
1	44	1
2	20	0
3	44	9
4	40	0
5	19	2
6	20	0
7	16	4

$\bar{X}$ = 29.0

$\bar{Y}$ = 2.29

t = 5.30, significant at the 5 percent level

TABLE 23. Algal Growth (turbidimetric Klett units) With and Without UO_2 (50 mg/50 ml culture medium); Organism is isolate AF 219 from Rocky Creek.

Flask #	x Control	y UO_2
1	11	15
2	18	13
3	23	16
4	31	18
5	30	22
6	16	20
7	20	34

$\bar{X} = 21.29$

$\bar{Y} = 19.71$

$t = 1.70$, not significant at the 5 percent level

TABLE 24. Algal Growth (turbidimetric Klett units) With and Without UO_2 (50 mg/50 ml culture medium); Organism is isolate AF 214 from Rocky Creek.

Flask #	x Control	y UO_2
1	44	15
2	20	29
3	44	33
4	40	15
5	19	34
6	20	25
7	16	49

$\bar{X}$ = 29.0

$\bar{Y}$ = 28.5

t = 2.43, significant at the 5 percent level

TABLE 25. Algal Growth (turbidimetric Klett units) With Dilutions of UO_2 in Culture Medium; Organism is isolate AF 214 from Rocky Creek.

Flask #	% Saturated UO_2 Culture Medium 100%	80%	60%	40%	20%	0% (control)
1	12	21	21	32	27	33
2	6	23	27	30	24	36
3	8	42	29	34	21	21
4	13	24	33	31	30	23
5	14	32	31	21	42	29
mean	10.6	28.4	28.2	29.6	28.8	28.4
t	*5.49	0	0.06	0.33	0.09	

*t = Significant at the 5 percent level

TABLE 26. Summary Table of Stage 2 Tests.

Culture Designation	Soluble U_3O_8 Conc., ppb. Inhibitory	Not Inhibitory	Soluble UO_2 Conc., ppb. Inhibitory	Not inhibitory
AF 37	6.9(sat.)-4.1	2.8	3.2(sat.)-2.6	1.9
AF 75			2.0(sat.)	1.6
AF 214			13.6(sat.)	10.9

TABLE 27. Uranium Uptake by Cells of Isolate AF 37 (Replicate 1).

SAMPLE	U_3O_8 IN MED., ORIGINAL CONC. ppb.	U_3O_8 IN CELLS, FINAL CONC. ppb.	UO_2 IN MED., ORIGINAL CONC. ppb.	UO_2 IN CELLS, FINAL CONC. ppb.	ACCUMULATION FACTOR
1	5.95	115			19.3
2	5.95	288			48.4
3			2.76	173	62.6
4			2.76	250	90.6

Samples 1 and 3: 0° C and darkness for 8 hours.

Samples 2 and 4: 20°C and illumination at 300 footcandles for 8 hours

TABLE 28. Uranium Uptake by Cells of Isolate AF 37 (Replicate 2).

SAMPLE	U_3O_8 IN MED., ORIGINAL CONC. ppb.	U_3O_8 IN CELLS, FINAL CONC. ppb.	UO_2 IN MED., ORIGINAL CONC. ppb.	UO_2 IN CELLS, FINAL CONC. ppb.	ACCUMULATION FACTOR
1	5.95	2675			449
2	5.95	3025			508
3	5.95	3637			611
4			2.76	787	285
5			2.76	1287	450
6			2.76	1900	688

Samples 1 and 4: 5 min. exposure of cells to uranium.

Samples 2 and 5: 0°C and darkness for 8 hours.

Samples 3 and 6: 20°C and illumination at 300 footcandles for 8 hours

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APPENDIX A

MOBILITY OF DEPLETED URANIUM BY DISSOLUTION IN NATURAL WATERS ON RANGE C-74

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INTRODUCTION

An attempt to quantitatively estimate the amount of depleted uranium removed or mobilized by natural waters represents a problem fraught with imprecision. Although the thermodynamic properties of uranium compounds and complexes are known with reasonable certainty, the chemical and physical conditions that exist on Range C-74 are largely unknown or such information is not available. As a consequence most of the effort for this project has been directed toward establishment and illustration of the stability limits for important uranium complexes and compounds. Thus, as more data become available from Range C-74 the solubility and mobility of uranium can be more accurately defined.

Some important works that discuss the geochemistry of uranium are: Miller (1958), Hostetler and Garrels (1962); Lopatkina (1964); Szalay (1964); and Doi (1975). The most recent and perhaps most important work to date is Langmuir (1978) in which the author presents a collection and critical evaluation of thermodynamic data for 30 minerals and other solids as well as for 42 dissolved uranium species. Langmuir's article has served as the sole source of thermodynamic data for this report. The several oxidation potential (Eh) versus pH diagrams presented in this report are recalculated modifications of similar diagrams presented in Langmuir (1958). The methods of calculation are described in works by Butler (1973), Garrels and Christ (1965), and Krauskopf (1967).

It is important to note that in geochemical calculations, electrode potentials more oxidizing than a hydrogen half-cell are positive and those more reducing than hydrogen are negative by convention. This is the inverse of the convention used in chemical literature such as Latimer (1964).

GEOCHEMICAL ENVIRONMENT OF RANGE C-74 AND ROCKY CREEK-DATA AND ASSUMPTIONS

The geologic units exposed in the vicinity of Range C-74 consist of gravels, sands, and clays of Miocene to Pleistocene age. (Yon and Hendry, 1969; and Marsh, 1966). These units collectively form a shallow "sand and gravel" aquifer system (Pascale, 1974). The Marianna Limestone of Oligocene age underlies the sands and gravels and is not exposed at the surface in this area, but has been encountered through drilling water wells.

Partial chemical analyses of water from wells drilled in the sand and gravel aquifer have been reported by Foster and Pascale (1971), and are summarized in Table A-1. Well numbers 30 and 31 have a higher pH and higher concentrations of calcium, bicarbonates, sulfate, silica, and potassium than the other wells. Therefore, wells 30 and 31 appear to receive water from the Marianna Limestone rather than the sand and gravel aquifer. Odum (1953) has presented evidence that the phosphate concentration of ground water in Walton County should be less than 0.05 part per million (ppm). The above data are used in this report to represent the general chemical characteristics of ground water in the vicinity of Range C-74. Data on the Eh (oxidation potential) of ground water are unavailable.

Information on the flow characteristics of Rocky Creek have been published by Heath and Wimberly (1971). Pascale (1974) reported a partial analysis of one sample of water from Rocky Creek which contained 3.8 ppm silica, 2 ppm bicarbonate, 0.2 ppm sulfate, 0.1 ppm fluoride, 0.06 ppm phosphate and had a pH of 6.2. The pH range of 56 measurements of water samples from Rocky Creek and Turkey Creek (O'Kelley, 1976) was 4.6 to 5.8. Dissolved oxygen in these samples varied from 3.4 to 9.4 ppm. Calculations based on these data indicate that the partial pressure of oxygen (P_{O_2} in Rocky Creek has a range of

Table A-1.

Partial Chemical Analyses of Water from Wells in the sand and gravel aquifer (from Foster and Pascale, p. 22 and p. 57, 1971)

Well Ref. No.	Depth	pH	Fe	SO_4	HCO_3	F	SiO_2	Ca^{++}	K^+
14	87	6.5	.32	2.2	13	0.1	5.1	4.0	0.2
15	65	6.3	.07	.8	2.	0	3.4	0.2	0.4
16	47	6.4	.26	.4	4	0	3.3	1.2	0.3
20	60	6.9	2.1	.4	12	0	4.2	0.6	0.0
21	165	6.9	.06	.4	6	0	7.7	0.6	1.4
22	90	5.9	.07	.2	6	.1	6.7	2.6	0.3
23	108	6.5	.22	.8	13	.1	5.5	0.6	0.0
24	104	6.3	.36	.4	10	0	1.9	1.4	0.0
25	106	6.6	.2	.4	6	0	9.3	0.3	0.5
26	110	5.8	--		6	0			
27	95		.17	.8		.1	5.2	0.6	0.2
30	58	7.1	.10	4.4	96	.1	22	18	2.4
31	65	8	.30	6	141	.1	15	26	2.3

$10^{-3.54}$ to $10^{-3.97}$ atm. Since

$$H_2O = \tfrac{1}{2}O_2 + 2H^+ + 2e^-$$
$$\text{where } E^{o}_{O_2} = +1.23 \text{ v}$$

then

$$Eh = 1.23 + 0.03 \log (P_{O_2})^{\frac{1}{2}} - 0.059 \text{ pH}$$

and the oxidation potential (Eh) of Rocky Creek should vary between 0.85v and 0.88v. However, measured oxidation potentials in nature are always less than those calculated by the above equation and are probably better represented by calculations of the empirical equation as modifed from Baas Becking et. al. (1960)

$$Eh = 1.05 + 0.03 \log (P_{O_2})^{\frac{1}{2}} - 0.059 \text{ pH}$$

which gives an Eh range of 0.71v to 0.75 v for Rocky Creek.

The average annual rainfall for the years 1975 through 1977 was 66.4 inches (Sandra Lefstadt, 1978, written communication). Based on the assumption that rain water equilibrates with oxygen and carbon dioxide in the atmosphere the following obtains

$$CO_2 + H_2O = H_2CO_3$$
$$\text{where } K = 10^{-1.467}$$

and
$$H_2CO_3 = H^+ + HCO_3$$
$$\text{where } K = 10^{-6.38}$$

Since the partial pressure of carbon dioxide in the atmosphere is $10^{-3.5}$ atm., the pH of rainwater should be approximately 5.7 and carbonic acid is the dominant carbonate bearing species in solution. The partial pressure of oxygen in the atmosphere is $10^{0.2}$atm., therefore, from the equation of Baas Becking et al. (1960) the maximum Eh of rainwater should be 0.70 v. at a pH of 5.7.

The P_{CO_2} in the soil zone commonly has values of 10^{-2} atm, which is significantly higher than in rainwater. As a result the pH of water in the soil zone may be 4.9.

In summary, the model from which the chemical behavior of uranium is calculated begins with slightly acidic (pH = 5.7) rainwater that is oxidizing (Eh = 0.7v) and contains some dissolved carbonate. Upon entering the soil zone the pH decreases to about 4.9, carbonate concentrations increase, and the Eh should decrease due to oxygen consuming reactions. Chemical reactions, as the water percolates downward into the sand and gravel aquifer, cause a rise in pH (5.9 to 6.9, Table A-1), a decrease in carbonate content, a continued decrease in Eh, and an increase in concentration of other dissolved constituents. If the water comes in contact with the Marianna Limestone it will become basic (pH of 7 to 8), have a high concentration of dissolved constituents, and may become reducing (Eh less than zero). Water in Rocky Creek is derived from ground-water flow, inflow, surface runoff, and direct precipitation. It has a pH range of 4.6 to 5.8, is less oxidizing than rain water, but more oxidizing than ground water, and has a lower total concentration of dissolved constituents than ground water.

AQUEOUS URANIUM SPECIES

Aqueous uranium species for which thermochemical data are available (Langmuir, 1978) are listed in Table A-2. Conditions that determine which uranium ion or complex is dominant are: oxidation potential (Eh), pH, as well as the presence and concentration of other chemical species with which uranium can complex. Elaboration in the following sections will reveal the basis for my opinion that the important aqueous uranium species in the area of Range C-74 are; U(IV) as U^{4+}, and uranus hydroxide complexes: U(V) as UO_2^+; and U(VI) as UO_2^{2+}, and uranyl hydroxide and carbonate complexes. Uranium also complexes strongly with fluoride, chloride, sulfate, phosphate, and silicate (see Table A-2).

Table A-2.

Aqueous Uranium Species
(From Langmuir, 1978)

Ions

U^{3+}	UO_2^{+}
U^{4+}	UO_2^{+2}

Hydroxides

UOH^{3+}	UO_2OH^{+}
$U(OH)_2^{2+}$	$(UO_2)_2(OH)_2^{2+}$
$U(OH)_4^{o}$	$(UO_2)_3(OH)_5^{+}$
$U(OH)_5^{-}$	

Fluorides

UF^{3+}	UO_2F^{+}
Uf^{2+}	$UO_2F_2^{o}$
UF_{3+}	UO_2F_3
UF_{4o}	$UO_2F_4^{2-}$
UF_5^{-}	
UF_6^{2-}	

Chlorides

UCl^{3+}	UO_2Cl+

Sulfates

USO_4^{2+}	UO_2SO_{4o}
$U(SO_4)_2^{o}$	$UO_2(SO_4)_2^{2-}$

Phosphates

$UHPO_4^{2+}$	$UO_2HPO_4^{o}$
$U(HPO_4)_2^{o}$	$UO_2(HPO_4)_2^{2-}$
$U(HPO_4)_3^{2-}$	$UO_2H_2PO_4+$
$U(HPO_4)_4^{4-}$	$UO_2(H_2PO_4)_2^{o}$
	$UO_2(H_2PO_4)_3^{-}$

Silicate

$UO_2SiO(OH)_3^{+}$

Carbonates

$UO_2CO_3^{o}$

$UO_2(CO_3)_2^{2-}$

$UO_2(CO_3)_3^{4-}$

However, these complexes do not significantly contribute to the concentration of uranium in solution near Range C-74.

Uranium Species of Relatively Low Importance

Fluoride Complexes

Uranus and uranyl fluoride complexes (Table A-2) may be important contributors to uranium solubility in acidic water. Uranus fluoride complexes have insignificant concentrations in solutions with a pH above 3.5 and the concentration of uranyl fluoride complexes become unimportant above pH 5. The maximum fluoride measured in water from the sand and gravel aquifer (Table A-1) was 0.1 ppm. The lowest pH from well water by Foster and Pascale (1971) was 5.8. Of 56 pH measurements from water in Rocky Creek and Turkey Creek, O'Kelley (1976) reported only four samples with a pH below 5. Because of the low fluoride concentrations and the pH of water in the area, uranium solubility is probably unaffected by fluoride complexing on Range C-74.

Chloride Complexes

Of all uranium complexes discussed by Langmuir (1978), chloride complexes are the weakest. Like the fluorides, uranus and uranyl chloride complexes should be most important in water that is more acidic than found on Range C-74.

Sulfate Complexes

Langmuir (1978) has demonstrated that $UO_2SO_4^0$ may constitute as much as 25 percent of the total dissolved uranium species at pH 5 when the total sulfate in solution is 100 ppm. The importance of this complex decreases at higher pH. The highest reported sulfate concentration in waters near Range C-74 is 6 ppm (Table A-1) and most values are less than one ppm. Therefore, it seems probable that, at maximum, $UO_2SO_4^0$ concentrations are two percent of the total dissolved uranium in the study area and that under most conditions this species represents less than 0.25 percent of the total dissolved uranium.

Phosphate Complexes

Among the most stable of all uranium complexes are those with phosphate. $UO_2(HPO_4)_2^{2-}$ can be a dominant uranium species in solution (pH 4 to 10) if the total phosphate concentration is 0.1 ppm or greater.

Little data exist on the concentration of phosphate in waters of the study area. Odum (1953) indicates that as a general rule, phosphate is less than 0.05 ppm in the western panhandle of Florida. One sample of water from Rocky Creek analyzed by Pascale (1974) contained 0.06 ppm phosphate. Since the most important uranium complex is $UO_2(HPO_4)_2^{2-}$ and this complex requires two moles of biophosphate for each uranyl group, then logic requires that the maximum expected UO_2^{2+} concentration that could complex with 0.05 ppm phosphate is $10^{-6.58}$ M/l or 0.07 ppm.

Silicate Complexes

The complex $UO_2SiO(OH)_3^+$ may represent as much as 50 percent of the total uranium concentration in solutions containing 60 ppm silica and total uranium of 10^{-8} M/l, at pH 6. Concentrations decrease appreciably at higher and lower pH (Langmuir, 1978). Because 10^{-8} M/l uranium equals 2.4 ppb, and except for wells penetrating the Marianna Limestone, the maximum silica content of water in the study area is less than 10 ppm; the maximum expected concentration of uranyl silicate complexes in solution is less than one part per billion.

Important Aqueous Uranium Species

Ions and Hydroxides of U(IV), U(V), and U(VI)

Figure A-1 represents the Eh-pH stability fields for U^{4+}, U^{5+} (as UO_2^+) U^{6+} (as UO_2^{2+}), and the uranus and uranyl hydroxide complexes. The upper and lower (dashed) boundaries represent the stability limits of water. The

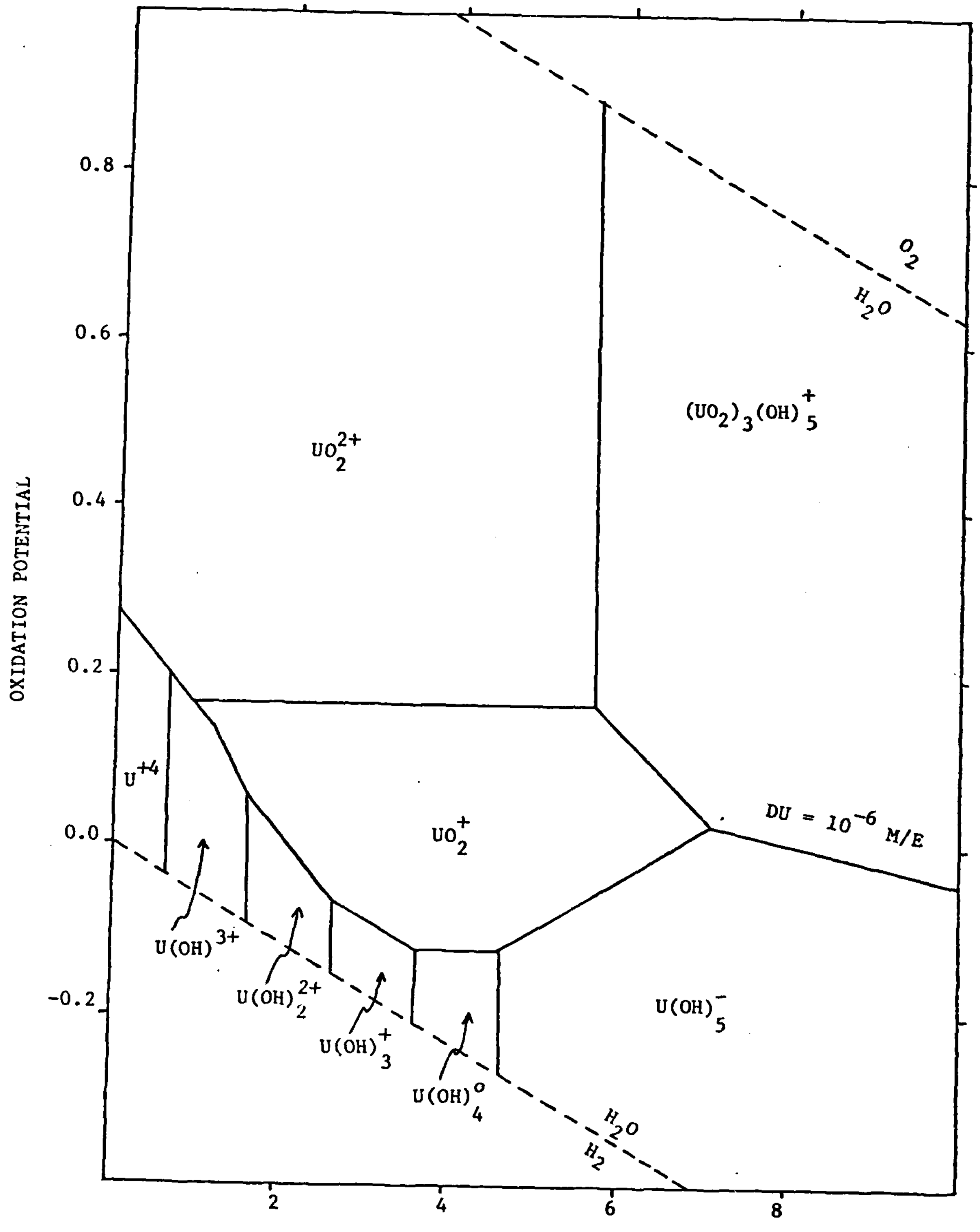

Figure A-1. Eh-pH Diagram for U^{+4}, UO_2^{2+} and Uranium Hydroxide Complexes boundaries separating adjacent fields represent the line along which complexes in the adjacent fields are present in equal concentrations. In pure water and in the absence of solid phases the complex listed in each stability field is the dominant complex in solution. The equations from which Figure A-1 was derived are listed in Appendix B. The thermodynamic data are given by Langmuir (1978).

The boundary between $U(OH)_5^-$ and $(UO_2)_3(OH)_5^+$ on Figure A-1 has a slope that depends on the total uranium concentration in solution (total uranium is 10^{-6} M/l on Figure A-1). As long as the solution is not saturated in uranium (no solid phases present) the other boundaries on Figure A-1 are not concentration dependent.

Carbonate Complexes

Figure A-2 represents the effects of the presence of carbonate in uranium-bearing solutions. The solid lines of Figure A-2 represent stability fields for carbonate complexes when the partial pressure of carbon dioxide is 10^{-2} atm. (carbon dioxide in the soil zone) and the dashed lines illustrate the same stability fields when the partial pressure of carbon dioxide is $10^{-3.5}$ atm. (atmospheric carbon dioxide).

The importance of Figure A-2 is that carbonate complexes are more stable than $(UO_2)_3(OH)_5^+$ and under some conditions are more stable than $U(OH)_5^-$.

As a general rule Figures A-1 and A-2 cannot be used to determine the centration of uranium in solution because of the absence of solid phases. However, the importance of these two figures should not be underestimated. The information contained therein will be used in a later section to demonstrate the possible transient existence of several of the complexes as metastable phases which allow migration of uranium from the 30 mm penetrators into the

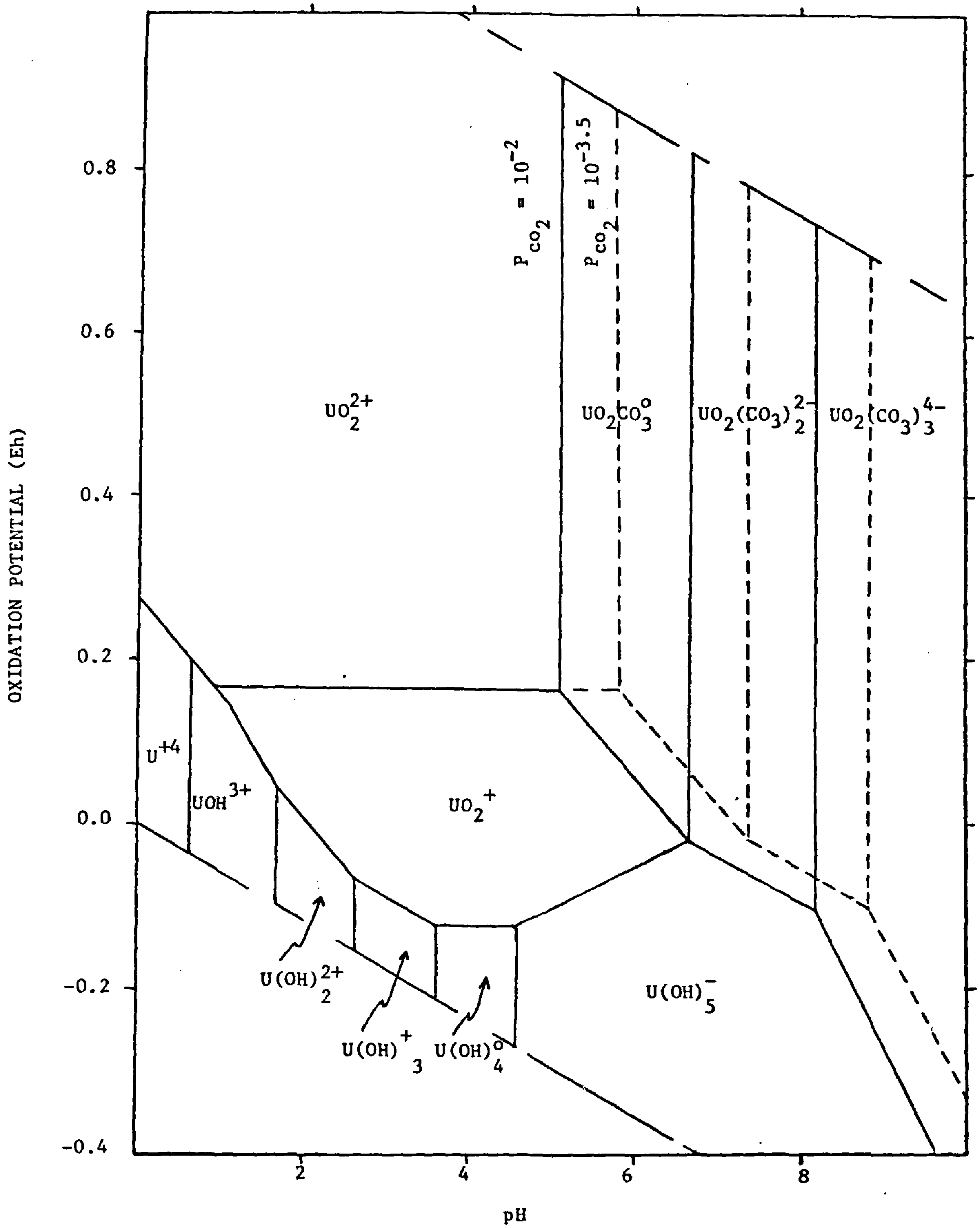

Figure A-2. Eh-pH Diagram for U^{+4}, UO_2^+, $UO_@^{2+}$, Uranus Hydroxide and Uranyl Carbonate Complexes.

surrounding earth material in the target butt.

EQUILIBRIA BETWEEN AQUEOUS URANIUM SPECIES AND URANIUM SOLIDS

Table A-3 lists the important solid uranium compounds (including minerals). It is obvious from the preceding discussion that compounds containing silica, fluoride, and phosphate should not be present on Range C-74. Within the pH range believed to exist in the study area (4.5 to 8) the minerals gummite (UO_3), schoepite ($UO_2(OH)_2 \cdot H_2O$), and rutherfordite (UO_2CO_3) should not be stable.

Uranium solids that should be present on Range C-74 include uranium metal (penetrators), UO_2 (uraninite), UO_2 (amorphous), U_4O_9, U_3O_8, and possibly $K_2(UO_2)_2(VO_4)_2$ (carnotite), and $Ca(UO_2)_2(VO_4)_2$ (tyuyamunite). Potassium and calcium concentrations in the water may be too low (see Table A-1) for production of the vanadate minerals. Vanadium concentrations in water of the study area are unknown.

Superimposing the stability field for uraninite on the Eh-pH diagram (Figure A-2) results in the configuration shown by Figure A-3. The boundaries between solid and aqueous uranium species are concentration dependent and in Figure A-3 represent an aqueous uranium concentration of 10^{-6} M/l (0.28 ppm) in equilibrium with uraninite. Figure A-4 is a similar Eh-pH diagram representing the stability field for uraninite in equilibrium with a dissolved uranium concentration of 10^{-9} M/l (0.28 ppb). Dashed lines on Figures A-3 and A-4 represent equilibria with solutions containing carbon dioxide partial pressures of $10^{-3.5}$ atm, and solid lines represent solutions with partial pressures of carbon dioxide of 10^{-2} atm.

It is apparent from Figures A-3 and A-4 that uranite is more stable (or less soluble) in solutions with a low carbonate content. Further comparison of the

Table A-3.

Solid Uranium Compounds (mineral names, where appropriate, are given in parentheses). From Langmuir (1978)

d-U

*UO_2 (uraninite)

UO_2 (am)

UO_3 (gummite)

*U_4O_9

U_3O_8

$USiO_4$ (coffinite)

UF_4

$UF_4 \cdot 2.5\ H_2O$

*$UO_2(OH)_2 \cdot H_2O$ (schoepite)

UO_2CO_3 (rutherfordite)

$U(HPO_4)_2 \cdot 4H_2O$

$CaU(PO_4)_2 \cdot 2H_2O$ (ningyoite)

$(UO_2)_3(PO_4)_2$

$H_2(UO_2)_2(PO_4)_2$ (H-autunite)

$Na_2(UO_2)_2\ (PO_4)_2$ (Na-autunite)

$K_2(UO_2)_2\ (PO_4)_2$ (K-autunite)

$(NH_4)_2(UO_2)_2(PO_4)_2$ (uramphite)

$Mg(UO_2)_2(PO_4)_2$ (saleeite)

$Ca(UO_2)_2(PO_4)_2$(autunite)

$Sr(UO_2)_2(PO_4)_2$ (sr-autunite)

$Ba(UO_2)_2(PO_4)_2$ (uranocircite)

$Fe(UO_2)_2(PO_4)_2$ (bassetite)

$Cu(UO_2)_2(PO_4)_2$ (torbernite)

$Pb(UO_2)_2(PO_4)_2$ (przheualskite)

$*K_2(UO_2)_2(VO_4)_2$ (carnotite)

$*Ca(UO_2)_2(VO_4)_2$ (tyuyamunite)

$Ca(UO_2)_2(SiO_3OH)_2$ (uranophane)

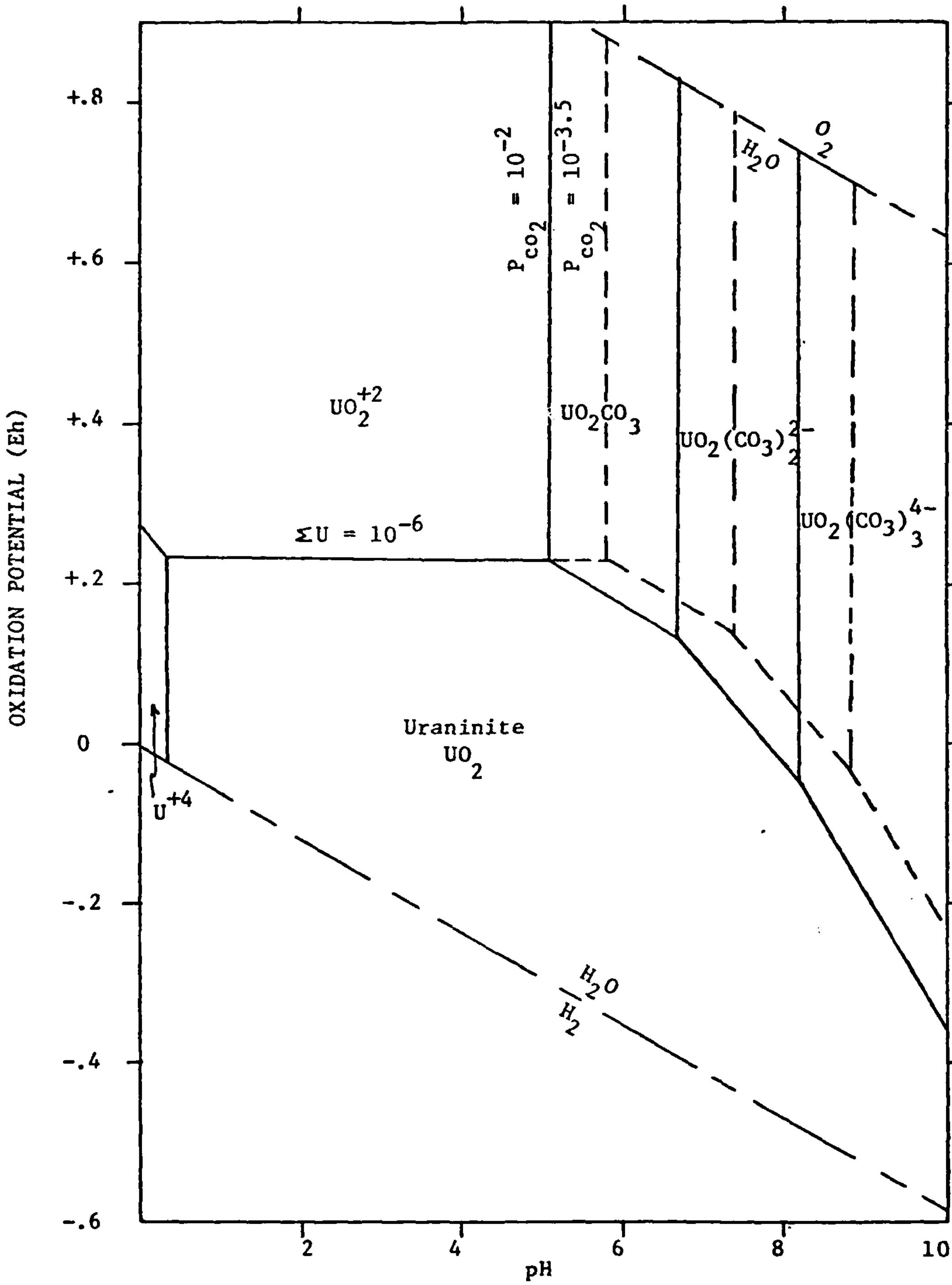

Figure A-3. Eh-pH Diagram for the System $U\text{-}O_2\text{-}CO_2\text{-}H_2O$ ($25^\circ C$)
$U = 10^{-6}$ (0.28 ppm).
$PCO_2 = 10^{-2}$ (solid lines)
$PCO_2 = 10^{-3.5}$ (dashed lines)

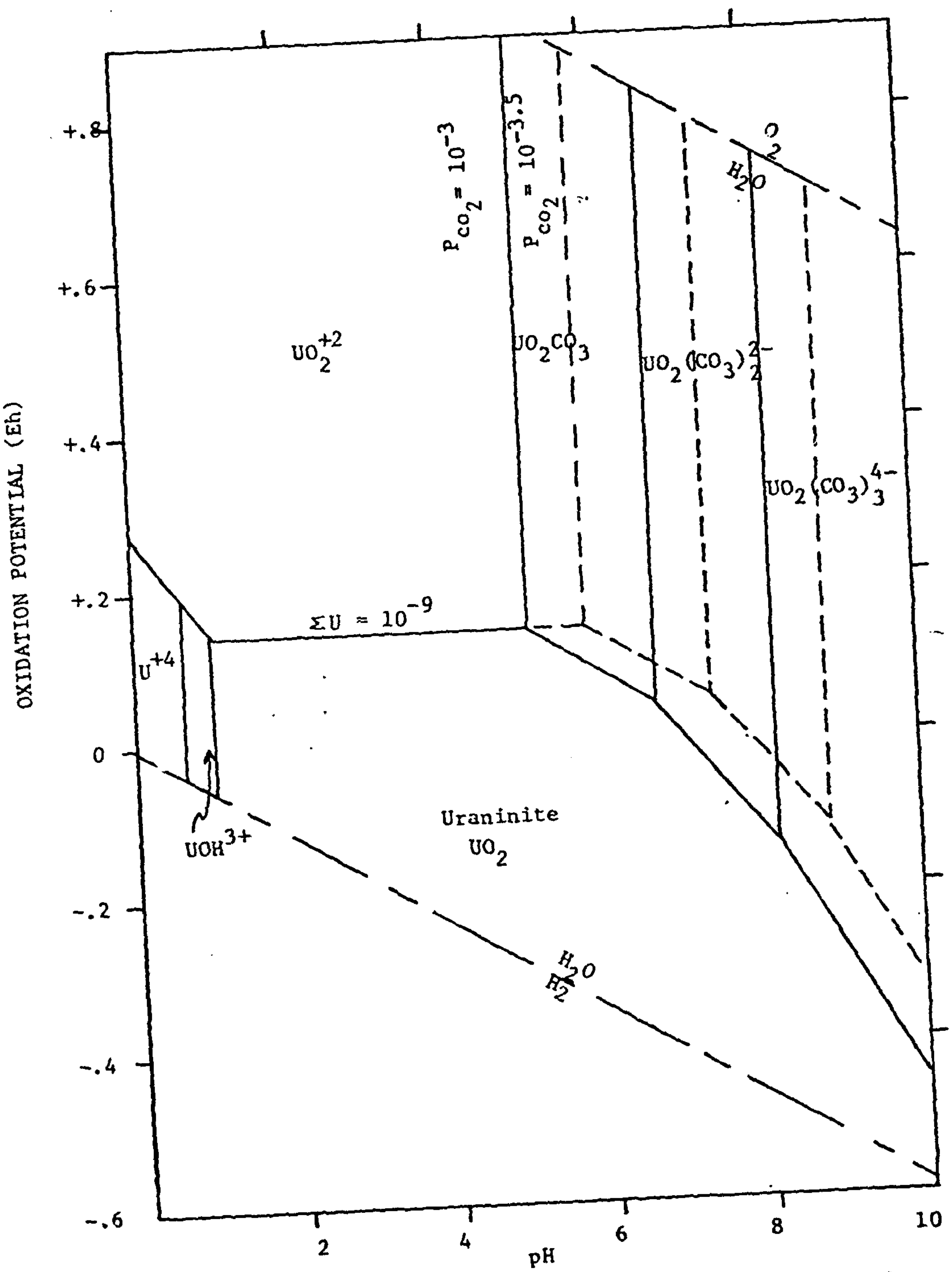

Figure A-4. Eh-pH Diagram for the System $U\text{-}O_2\text{-}CO_2\text{-}H_2O$ (25°C)
$U = 10^{-9}$ M/e (0.28 ppm)
$PCO_2 = 10^{-2}$ (solid lines)
$PCO_2 = 10^{-3.5}$ (dashed lines)

two figures indicates that the uraninite stability field expands as the concentration of uranium in solution increases.

At aqueous uranium concentrations of 10^{-6} M/l or greater and carbon dioxide partial pressures of $10^{-3.5}$ or greater U_4O_9 and U_3O_8 would become additional stable phases on Figure A-3.

Water on Range C-74 should have a pH between 4.5 and 7. Under these conditions the Eh must be maintained near zero (see Figure A-4) in order to reduce the uranium, cause fixation as uraninite, and assure that effluent water has uranium concentrations near 10^{-9} M/l. There is no evidence that, under present conditions, an Eh near zero exists in the target butt material on Range C-74.

Under oxidizing conditions in the intermediate pH range Langmuir (1978) has shown that amorphous ferric oxyhydroxides can adsorb uranyl ions and reduce the uranium concentration in solution to one to two ppb. If potassium is present (39 ppm) in association with limited amounts of vanadium (0.1 ppm) carnotite precipitation can also reduce the uranium concentration in oxydizing solutions to the ppb range.

In my opinion the above evidence substantiates the conclusion that effluent water from Range C-74 has a uranium concentration in the low ppb range. Further consideration of the evidence, however, indicates that within the confines of the target butt material, the soil zone, and perhaps in the sand and gravel aquifer of Range C-74 uranium has a significant mobility and is intermittently to continuously being dissolved and reprecipitated. This process can cause a gradual dispersal of uranium from the source area for an unknown distance into the surrounding earth materials, and may cause a continuously increasing loss of uranium from the target range.

Hanson (1974) concluded that depleted uranium has a lower solubility than natural uranium compounds. Even if this were true the depleted uranium is chemically unstable in the presence of water. The depleted uranium metal in the penetrators will begin reaction on contact with water. The metal will oxidize to U^{4+}, hydrolize water to form uranus hydroxide complexes which move downward with percolating rain water. Further oxidation to UO_2^+ will allow mobility. Even under reducing conditions the above complexes may move for some distance before precipitating as uraninite or the more soluble UO_2 (amorphous) solid. With each rainfall more uranium is leached from the penetrators and the UO_2 solids are partially remobilized. Under oxidizing conditions existing in the target butts U^{4+} complexes and solids can be oxidized to uranus complexes which are mobile unless and until fixed by sorption or as vanadate minerals. As a result of these processes uranium must be continuously dispersed outward and downward from the target butts.

SUMMARY

Limited analytical and empirical evidence indicates that waters associated with Range C-74 should have a usual pH range of 4.6 to 7, an Eh of 0.7 v. to 0.0, and contain limited quantities of dissolved constituents. In this pH range when the Eh is near zero depleted uranium metal in the penetrators will react with and hydrolize water to form uranus hydroxide complexes. The complexes will move with the water flow into surrounding areas and be precipitated as uraninite (UO_2) or as amorphous UO_2. Under more oxidizing conditions uranium is mobilized as uranyl complexes (UO_2^{2+} and $UO_2CO_3^o$) and will be fixed by sorption on ferric oxyhydroxide compounds or precipitated as carnotite if sufficient potassium and vanadium are present. In either case the concentration of uranium in water escaping Range C-74 (neglecting overland flow) should be in the low part per billion range.

APPENDIX B

Eh-pH

Stability Fields

Uranus Hydroxide Complexes 25°C

$U^{4+} + H_2O = U(OH)^{3+} + H^+$ Log K = 0.628

$U(OH)^{3+} + H_2O = U(OH)_2^{2+} + H^+$ Log K - -1.581

$U(OH)_2^{2+} + H_2O + U(OH)_3^{+} + H^+$ Log K = -2.608

$U(OH)_3^{+} + H_2O = U(OH)_4^{o} + H^+$ Log K = -3.634

$U(OH)_4^{o} + H_2O = U(OH)_5^{-} + H^+$ Log K = -4.587

Eh-pH

U^{+5} Stability Field

$UO_2^+ = UO_2^{+2} + e^-$ Log K = -2.786 $E^o = 0.165$

$U(OH)^{3+} + H_2O = UO_2^+ + 3H^+ + e^-$ Eh = 0.341 -0.177 pH

$U(OH)_4^o = UO_2 + 2H_2O + e^-$ $E^o = -0.124$

$U(OH)_5^- + H^+ = UO_2^+ + 3H_2O + e^-$ Eh = -0.397 + 0.059 pH

$3UO_2^+ + 5H_2O = (UO_2)_3(OH)_5^+ + 5H^+ + 3e^-$

$Eh = 0.472 + 0.02 \log [(UO_2)_3(OH)_5^+ - 0.059\ UO_2^+] - 0.098\ pH$

Eh-pH Stability Fields

Uranium Carbonate Complexes

$UO_2^+ + H_2CO_3 = UO_2CO_3 + 2H^+ = e^-$

$Eh = 0.556 - 0.059 [H_2CO_3] - 0.118pH$

$U(OH)_5^- + 2H_2CO_3 \quad UO_2(CO_3)_2^{2-} + 3H_2O + H^+ + e^-$

$Eh = -0.015 - 0.118 [H_2CO_3] - 0.059 pH$

$UO_2^{2+} + H_2CO_3 = UO_2CO_3^o + 2H^+ \quad \log K = -6.628$

$pH = 0.5 \log K + 0.5 \log [H_2CO_3]$

$UO_2CO_3^o + H_2CO_3 = UO_2(CO_3)_2^{2-} \quad \log K = -9.78$

$pH = 0.5 \log K + 0.5 \log [H_2CO_3]$

$UO_2(CO_3)_2^{2-} + H_2CO_3 = UO_2(CO_3)_3^{4-} + 2H^+ \quad \log K = -12.273$

$pH = 0.5 \log K + 0.5 \log [H_2CO_3]$

$UO_2 + H_2CO_3 = UO_2CO_3^o + 2H^+ + 2e^-$

$Eh = 0.605 + 0.03 \log [UO_2CO_3^o] - 0.03 \log [H_2CO_3] - 0.059 pH$

$UO_2 + 2H_2CO_3 = UO_2(CO_3)_2^{2-} + 4H^+ \pm 2e^-$

$Eh = 0.894 + 0.03 \log [UO_2(CO_3)_2^{2-}] - 0.059 \log [H_2CO_3] - 0.118pH$

$UO_2 + 3H_2CO_3 = UO_2(CO_3)_3^{4-} + 6H^+ + 2e^-$

$Eh = 1.256 + 0.03 \ UO_2(CO_3)_3^{4-} - 0.089 \log [H_2CO_3] - 0.177 pH$

Eh-pH Uraninite Stability Field.

$U^{+4} + 2H_2O = UO_2 + 4H^+$ Log K = 4.638

$pH = 1.16 + 0.25 \log [U^+]$

$UO_2 = UO_2^+ + e^-$

$Eh = 0.654 + 0.059 [UO_2^+]$

$UO_2 = UO_2^{2+} + 2e^-$

$Eh = 0.409 + 0.03 \log [UO_2^{2+}]$

$UO_2 + H_2CO_3 = UO_2CO_3 + 2H^+ + 2e$

$Eh = 0.605 + 0.03 \log [UO_2CO_3] - 0.03 \log [H_2CO_3] - 0.059\ pH$

$UO_2 + 2H_2CO_3 = UO_2(CO_3)_2^{2-} + 4H^+ + 2e^-$

$Eh = 0.894 + 0.03 \log [UO_2(CO_3)_2^{2-}] - 0.059 [H_2CO_3] - 0.118\ pH$

$UO_2 + 3H_2CO_3 = UO_2(CO_3)_3^{4-} + 6H^+ + 2e^-$

$Eh = 1.256 + 0.03 [UO_2(CO_3)_3^{4-}] - 0.089 [H_2CO_3] - 0.177\ pH$

Carbonate Equilibria

$$CO_2 + H_2O = H_2CO_3 \qquad \log K = -1.467$$

$$[H_2CO_3] = 10^{1.467} P_{CO_2}$$

$$H_2CO_3 = HCO_3^- + H^+ \qquad \log K = -6.38$$

$$HCO_3^- = CO_3^{=} + H^+ \qquad \log K = -10.3$$

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